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(54) Title: **METHOD OF MAKING A FOAMED HYDRAULIC BINDER BASED PRODUCT**

(57) Abstract: A method of making a composite product includes the steps of mixing a hydraulic binder and water to form a paste and then introducing a foam into the paste to form a foamed product. The foam is generated from a mixture of a polyvinyl alcohol solution and a second hydrophilic polymer such as gelatin. The foamed product is formed into a desired shape and the hydraulic binder is allowed to set to form the composite product.

METHOD OF MAKING A FOAMED HYDRAULIC BINDER BASED PRODUCT

BACKGROUND OF THE INVENTION

This invention relates to a method of making a product from a hydraulic binder and a foam, and to the product so made.

Foams generated from organic compound solutions in water, for addition to pastes formed from a hydraulic binder and water, are known. Examples of suitable organic compounds for the manufacture of such foams are polyvinyl alcohols, various surface active agents and proteinaceous compounds. Foamed hydraulic binder products produced from these foams tend to suffer from foam instability. This in turn leads to foams with a large or irregular cell size, which in turn leads to variable density through the thickness of the final product, limitations as to product density control, and to the danger of foam collapse during processing.

On the other hand, when a foam is used which leads to a very fine cellular structure, then the resulting product has excellent thermal, acoustic and fire protection properties. Further the product can easily be nailed, sawn or worked, and may have a density as low as 200 kg/m³.

CONFIRMATION COPY

PCT Patent Application No PCT/GB 98/03556 to Windsor Technologies Limited teaches a method of making a composite product by mixing together a hydraulic binder, finely divided lignocellulosic fibres in an amount of from 1% to 30% inclusive by mass of the hydraulic binder, and water optionally containing a polyvinyl alcohol, the water being present in an amount sufficient to form a paste. There is then introduced into this mixture a foam generated from a polyvinyl alcohol, in an amount of from 0,05% to 15% inclusive by mass of the paste, and this is mixed to form a foamed product. The foamed product is formed into a desired shape and the hydraulic binder is allowed to set to form the composite product.

There is however always a need for new products formed from a hydraulic binder and a foam.

SUMMARY OF THE INVENTION

According to a first aspect of the invention there is provided a method of making a composite product including the steps of:

- (a) mixing:
 - (i) a hydraulic binder; and
 - (ii) water, optionally containing a polyvinyl alcohol, the water being present in an amount sufficient to form a paste;
- (b) introducing a foam into the paste in an amount of from 2% to 50% inclusive by mass of the paste, preferably in an amount of from 25% to 40% inclusive by mass of the paste, the foam being generated from a mixture of a polyvinyl alcohol solution and a second hydrophilic polymer, and mixing to form a foamed product;
- (c) forming the foamed product into a desired shape; and
- (d) allowing the hydraulic binder to set to form the composite product; the composite product being formed in the absence of thermosetting resin.

It is to be noted that the product is formed in the absence of a thermosetting resin. In other words the product contains no thermosetting resin.

According to a second aspect of the invention there is provided a product made by the method set out above.

DESCRIPTION OF EMBODIMENTS

The crux of the invention is a method of making a product, such a building board. The first step comprises mixing a hydraulic binder and water, optionally containing a polyvinyl alcohol and optionally containing a second hydrophilic polymer, the water being present in an amount sufficient to form a paste. There is then introduced into the paste a foam in an amount of from 2% to 50% inclusive by mass of the paste, and mixing to form a foamed product. The foam is generated from a mixture of a polyvinyl alcohol solution and a second hydrophilic polymer. Thereafter, the foamed product is formed into a desired shape and the hydraulic binder is allowed to set to form the product.

The first component of the product is a hydraulic binder. The hydraulic binder may be selected from the group consisting of a hydraulic cement, such as a Portland cement, e.g ordinary Portland cement or rapid hardening Portland cement, a calcium sulfoaluminate cement, a high alumina cement such as is used in refractory applications, a gypsum cement, calcium sulphate hemihydrate in either the alpha or beta form; magnesium oxychloride, magnesium oxysulphate, an alkali silicate such as sodium silicate and pozzolans such as ground granulated blast furnace slag and mixtures of two or more thereof.

The preferred hydraulic binders are a Portland cement such as ordinary Portland cement; a high alumina cement; a blend of a Portland cement and

a high alumina cement; and gypsum, i.e calcium sulphate hemihydrate in either the alpha or beta form, preferably the beta form.

When the hydraulic binder is a Portland cement, rapid gelation of the foamed hydraulic binder may be induced by adding, between steps (b) and (c), a gelation agent such as a high alumina cement-in-water paste or a sodium or potassium silicate in water solution. Using these gelation agents, gelation of the foam may be achieved within a few seconds of addition, and thus the addition of the gelation agent must be synchronized with process requirements.

accelerates

An example of a suitable high alumina cement for use as the hydraulic binder is Cement Fondu Lafarge containing approximately 40% by weight of aluminium oxide (alumina). This may optionally be blended with a Portland cement, for example in an amount of 10 parts of high alumina cement : 90 parts of a Portland cement to 90 parts of high alumina cement : 10 parts of a Portland cement. The higher the proportion of high alumina cement in the blend, the more refractory is the resulting foamed product. Burning out of the organic components of the composition at temperatures exceeding 700°C for a period exceeding 60 minutes may be carried out after setting and drying of the product, to produce a refractory product.

When using a sodium silicate as a gelation agent, it will generally be added in an amount of between 1% and 7% by mass of the mass of the Portland cement.

The hydraulic binder is mixed with water, preferably containing a polyvinyl alcohol in an amount of from 0,5% to 10% inclusive, preferably in an amount of from 1% to 5% inclusive of the polyvinyl alcohol by mass on the mass of the water.

The polyvinyl alcohol serves to compatibilise the hydraulic binder paste with the foam when it is added. It also serves as a colloidal protector stabilizing the foam, and as a polymer, it reinforces the resulting product.

The polyvinyl alcohol which is mixed with the water is preferably a low viscosity partially hydrolysed polyvinyl alcohol such as Mowiol 4/88 by Clariant.

The paste water may also contain a hydrophilic polymer which may be the same as or different from the second hydrophilic polymer.

The paste water, optionally containing the polyvinyl alcohol and the hydrophilic polymer is mixed with the hydraulic binder in an amount sufficient to form a paste.

The next step of the method of the invention is to produce a foam from a mixture of a polyvinyl alcohol in water solution and a hydrophilic polymer.

Preferably the polyvinyl alcohol is dissolved in water to form a solution containing from 1% to 10% inclusive, more preferably from 2% or 2,5% to 7% inclusive by mass of the polyvinyl alcohol to the total mass of the solution.

The polyvinyl alcohol used in the preparation of the foam is preferably a higher viscosity polyvinyl alcohol such as Mowiol 18/88 by Clariant. The preferred viscosity of the polyvinyl alcohol solution at a 5% concentration at 20°C is in the range 8mPa.s to 100mPa.s, the ideal being 50mPa.s which is the viscosity of Mowiol 18/88.

Mowiol 4/88 and Mowiol 18/88 have a degree of hydrolysis of 87,7 mol percent, and ester value of mgKOH per g of 140, and a residual acetal content of 10,7% by weight.

The solution from which the foam is produced also contains an amount of a second hydrophilic polymer, preferably an amount of from 0,2% to 5% inclusive, more preferably an amount of from 0,3% to 1,5% inclusive by mass of the second hydrophilic polymer to the total mass of the solution.

The second hydrophilic polymer is preferably a macromolecular colloidal protector which is either water soluble or water swellable, e.g. a hydrogel, which controls viscosity, thixotropy and rheology of the wet foamed hydraulic binder composition, acting synergistically with the polyvinyl alcohol to impose foam stability and minimise cell size.

The second hydrophilic polymer is preferably selected from the group:

- A. Natural polymers such as:
- (i) carbohydrates, i.e. modified starches such as the polyhydroxy pre-polymers;
 - (ii) natural carbohydrate gums, i.e. guar, or seaweed colloids, i.e. agar;
 - (iii) proteins such as gelatin;
- B. Semi-synthetic polymers such as:
- (i) the cellulose ethers, particularly sodium carboxymethyl celluloses or hydroxyethyl celluloses;
 - (ii) microbial gums such as xanthan gum;
- retarders* ✓ C. Synthetic polymers such as:
- (i) hydrogels such as the homo polymer and copolymer derivatives of acrylic and methacrylic acid, or a polyacrylamide-polyacrylate co-polymer;
 - (ii) polyacrylamide hydrophilic polymers.

Particularly suitable hydrophilic polymers are those soluble in water at elevated temperatures i.e. above 35°C and which gel at lower temperatures.

The preferred second hydrophilic polymer is gelatin, which is a proteinous macromolecule derived from collagen, which is the protein of skin, bones and connective tissues of animals. Gelatin may be obtained in a range of molecular sizes and shapes with a broad molecular weight distribution of

from 15 000 to 250 000. It is characterised by its viscosity in hot water in which it is soluble, and its phenomenon of gelling on cooling, its action as a protective colloid, its propensity to foam, its function as a binder and its synergy with polyvinyl alcohol.

In step (b) of the method of the invention, the foam is preferably generated by injecting air into a moving stream of the solution of the polyvinyl alcohol and the second hydrophilic polymer. Alternatively, the solution containing the polyvinyl alcohol and the second hydrophilic polymer may be atomized with air.

When the second hydrophilic polymer is gelatin, the solution of the polyvinyl alcohol and gelatin in water is preferably formed at an elevated temperature and kept at that elevated temperature up to and including the stage at which the foam is generated therefrom and introduced into the paste which is at ambient temperature. By elevated temperature there is meant a temperature in the range of from 35°C to 95°C. Immediately upon introduction of the foam into the paste, the gelatin gels to form a stable foam of very fine cell size, after which the hydraulic binder is allowed to set to form the final product.

Agar exhibits a similar phenomenon at concentrations as low as 0,5%.

Various additional components may be added to the mixture as set out below.

A suitable thixotropic agent or rheological controller may be added to the paste before the introduction of the foam, or to the solution from which the foam is generated. Examples of suitable agents of this type include high density polyethylene fibrils of bulk density less than 50 grams per litre, with or without an amorphous silica such as Stewathix by Schwarzwald Textilverke; fumed silica such the Aerosils by Degussa; bentonite; hollow glass balloons; added in an amount of about 1% or less on the mass of the hydraulic binder.

A suitable gelation agent may also be added, particularly in the case of Portland cements, as set out above.

When the hydraulic binder includes a high alumina cement, a suitable accelerator may be added such as for example lithium carbonate in an amount of from about 0,1% to about 0,8% inclusive by mass on the mass of the high alumina cement.

In order to minimise the sensitivity of gypsum foams to high atmospheric humidity, silicone water repellents or hydrophobic agents may be added to the hydraulic binder paste before the addition of the foam. Those preferred are the anhydrous silicones based on hydrogen-polysiloxane, added to the gypsum paste at the level of 0,1% to 0,5% on the mass of the gypsum. At an addition rate of 0,25% subsequent water absorption on submersion of a gypsum foam acoustic ceiling panel is reduced from of the order of 50% to below 5%, in this way avoiding any tendency to sag with increasing humidities. An example of a suitable product is Silicone Masonry Water Repellent BS94 by Wacker. Cohesion property of the composite is also improved, particularly at lower densities.

The paste may also include an amount of reinforcing fibres which preferably have a high aspect ratio, the fibres having lengths of from 1mm to 6mm, more preferably from 1,5mm to 4mm and preferably chosen from the group consisting of polyacrylonitrile, polyvinyl alcohol, polyester, polyethylene, polypropylene, glass fibre, ceramic fibre, mineral wool, aramid, or naturally occurring fibrous or high aspect ratio minerals such as wollastonite.

The composition may also contain reinforcing particles such as mica, phlogopite, delaminated exfoliated vermiculite such as FPSV by W R Grace, these particles having a diameter of less than 0,75mm, preferably less than 0,25mm.

Such reinforcing fibres or particles are preferably added in an amount of from 0,1% to 2%, more preferably in an amount of from 0,25% to 1,5% by mass of the mass of the hydraulic binder.

Suitable inorganic compounds, in small particles sizes may also be added to the hydraulic binder pastes, such as for example a silica flour, a talc, calcium carbonate, a diatomaceous earth and the like.

In addition, contributors to syntactic elements within the foam may be included in the hydraulic binder paste, such as for example an expanded mineral, e.g perlite, clays, aluminas, vermiculites, hollow glass balloons and silica fumes, or expanded organic particles such as ground or milled polymer foams such as polyurethanes, polyvinyl chlorides, or polystyrenes.

In step (c) of the method of the invention, the foamed product is formed into a desired shape, for example by conventional techniques such as casting or pouring or otherwise dispensing into a suitable mould or onto a moving belt or the like.

In step (d) of the method of the invention, the hydraulic binder is allowed to set to form the final product.

Thereafter, the final product may be used directly or may be cured and dried and thereafter machined into suitable sizes and the like.



The essential feature of the method of the invention is the use of a combination of a polyvinyl alcohol and a second hydrophilic polymer, which work synergistically together to produce the foam. Both the polyvinyl alcohol and the second hydrophilic polymer are colloidal protectors working together to encapsulate tiny bubbles of air and preventing their coalescence, thus maintaining foam stability and keeping the heavier particles of hydraulic binder in uniform suspension.

When the second hydrophilic polymer is a gelatin, the hot foam is added to the paste which is at ambient temperature. The gelatin fraction gels,

"freezing" the foam whilst the polyvinyl alcohol maintains the liquid, workable nature of the foam before setting of the hydraulic binder.

Both components, but particularly the polyvinyl alcohol, improve the mechanical properties of the set foam, which cannot be achieved with conventional foaming agents.

Examples of the invention will now be given.

Example 1

- A. A solution of 1 000 units by weight of water including 40 units by weight of Mowiol 18/88 polyvinyl alcohol by Clariant, and 15 units by weight of gelatin, is prepared at a temperature of 75°C.
- B. A hydraulic binder paste comprising of 2 000 units by weight of Portland cement, 600 units by weight of a 3% solution of Mowiol 4/88 polyvinyl alcohol-in-water by Clariant, 15 units by weight of Dolanit acrylonitrile fibres having a length of 3mm and a diameter of 27 microns with 500 000 fibres per gram, and 200 units by weight of undensified silica fume, are blended at ambient temperature.
- C. The mixture from step A is converted into a foam by the atomisation of air in the solution in a foam generator and the foam is added to the hydraulic binder paste from step B at the rate of 500 units by weight and mixed thoroughly.
- D. Immediately 75 units by weight of Silchem 3379 sodium silicate of a composition of silicon dioxide 29%, sodium oxide 8%, at a solids-in-water percentage of 37.88, and a weight ratio of silicon to sodium of 3.3:1, is added to the foamed hydraulic binder and thoroughly blended.
- E. The foam is spread upon a moving belt to a thickness of 25mm whereupon it immediately gels followed by curing accelerated if necessary by steam, to produce a final product.

Where autoclaving is selected as the cure method the Portland cement percentage of the composite is about 800 units by weight and a fine silica

flour typically a 300 mesh, i.e ground silica sand is included at about 1 200 units by weight. The gelled composite is cured after 24 hours precure in an autoclave at 180°C at elevated pressures of up to 10 bar for fourteen hours giving a cured product capable of being nailed with a total organic percentage in the composite of less than 2,5%.

The open cellular structure allows for the drainage of water after water wetting, the product is inflammable, is proof to biological degradation and is suitable for roof under-lays, floor under-lays, exterior siding, bath backer boards and the like, with densities in the range 300 to 900 kg/m³, exhibiting good thermal and acoustic insulation properties, good mechanical properties and reduced cost of distribution.

Example 2

- A. A solution of 4% by weight of Mowiol 18/88 polyvinyl alcohol by Clariant and 0, 75% by weight of polyacrylamide by PRP Resins, South Africa, in 500 units by weight of water is prepared at ambient temperature.
- B. A hydraulic binder paste comprising of 2 000 units by weight of the beta hemihydrate of calcium sulphate, 1 400 units by weight of a 3% in water solution of Mowiol 4/88 polyvinyl alcohol by Clariant is made.
- C. The polyvinyl alcohol/polyacrylamide solution is foamed in a foam generator by the atomisation of air in the solution to produce a low bulk density "dry" foam which is added to the paste from step B at the rate of 600 units by weight.
- D. The foamed hydraulic binder is spread on a moving belt to a thickness of 50mm, allowed to set and subsequently dried to produce a fire protection composite suitable for door cores, panel cores and the protection of steel from fire by fabricated encapsulation.

Example 3**Foam Stability Trials**

475 grams of the follow three solutions were foamed and the foam volume measured immediately and then again after standing for two and a half hours at 22°C:

- A. Polyvinyl alcohol Mowiol 18/88 at 5% concentration in water.
- B. Polyvinyl alcohol Mowiol 18/88 at 4% concentration in water plus polyacrylamide at 2% concentration.
- C. Polyvinyl alcohol Mowiol 18/88 at 4% concentration plus 2% of gelatin in water at 70°C.

Result:

Solution	Volume in cm ³ immediately after foaming	Volume in cm ³ after 2½ hours at 22°C	Foam volume reduction
A	2419	0	100%
B	2083	1747	16%
C	4839	4301	11%

CLAIMS

1. A method of making a composite product including the steps of:
 - (a) mixing:
 - (i) a hydraulic binder; and
 - (ii) water in an amount sufficient to form a paste;
 - (b) introducing a foam into the paste in an amount of from 2% to 50% inclusive by mass of the paste, the foam being generated from a mixture of a polyvinyl alcohol solution and a second hydrophilic polymer, and mixing to form a foamed product;
 - (c) forming the foamed product into a desired shape; and
 - (d) allowing the hydraulic binder to set to form the composite product; the composite product being formed in the absence of a thermosetting resin.
2. A method according to claim 1 wherein in step (b) the foam is added to the paste in an amount of from 25% to 40% inclusive by mass of the paste.
3. A method according to claim 1 or claim 2 wherein in step (b) the foam is generated from a mixture of a polyvinyl alcohol solution containing from 1% to 10% inclusive by mass of the polyvinyl alcohol to the total mass of the solution, and a second hydrophilic polymer in an amount of from 0,2% to 5% inclusive by mass of the second hydrophilic polymer to the total mass of the solution.
4. A method according to claim 3 wherein in step (b) the foam is generated from a mixture of a polyvinyl alcohol solution containing from 2,5% to 7% inclusive by mass of the polyvinyl alcohol to the total mass of the solution and from 0,3% to 1,5% inclusive by mass of the second hydrophilic polymer to the total mass of the solution.

- 5 A method according to any one of claims 1 to 4 wherein the second hydrophilic polymer is a polymer which is soluble in water at a temperature above 35°C and which gels at a lower temperature.
- 6 A method according to claim 5 wherein the second hydrophilic polymer is gelatin.
- 7 A method according to claim 6 wherein in step (b), a solution of polyvinyl alcohol and gelatin in water is formed at a temperature of from 35°C to 95°C, and in that the solution is maintained at this temperature until it is introduced into the paste and mixed to form the foamed product.
- 8 A method according to any one of claims 1 to 7 wherein in step (a)(ii), the water contains from 0,5% to 10% inclusive of a polyvinyl alcohol.
- 9 A method according to any one of claims 1 to 8 wherein in step (a)(ii) the water contains a hydrophilic polymer which may be the same as or different from the second hydrophilic polymer.
- 10 A method according to any one of claims 1 to 9 wherein in step (a)(i) the hydraulic binder is selected from the group consisting of a hydraulic cement, a calcium sulphoaluminate cement, a high alumina cement, a gypsum cement, calcium sulphate hemihydrate in either the alpha or beta form, magnesium oxychloride, magnesium oxysulphate, an alkali silicate, and a pozzolan, and a mixture of two or more thereof.
- 11 A method according to claim 10 wherein in step (a)(i) the hydraulic binder is selected from the group consisting of a Portland cement, a high alumina cement, a blend of a Portland cement and a high alumina cement, and calcium sulphate hemihydrate in either the alpha or beta form.

- 12 A method according to any one of claims 1 to 11 wherein in step (a) there is mixed into the paste an additional component selected from the group consisting of a gelation agent; a thixotropic agent or rheological controller; an accelerator; a silicone water-repellent; reinforcing fibres, reinforcing particles; and a contributor to syntactic elements within the foam; and a mixture of two or more thereof.
- 13 A composite product made by a method which includes the steps of:
- (a) mixing:
 - (i) a hydraulic binder; and
 - (ii) water in an amount sufficient to form a paste;
 - (b) introducing a foam into the paste in an amount of from 2% to 50% inclusive by mass of the paste, the foam being generated from a mixture of a polyvinyl alcohol solution and a second hydrophilic polymer, and mixing to form a foamed product;
 - (c) forming the foamed product into a desired shape; and
 - (d) allowing the hydraulic binder to set to form the composite product; the composite product being formed in the absence of a thermosetting resin.
- 14 A composite product according to claim 13 wherein in step (b) the second hydrophilic polymer is gelatin.
- 15 A composite product according to claim 13 or claim 14 wherein in step (b) the foam is introduced into the paste in an amount of from 25% to 40% inclusive by mass of the paste.

INTERNATIONAL SEARCH REPORT

Inte. onal Application No

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	--- CHEMICAL ABSTRACTS, vol. 85, no. 8, 23 August 1976 (1976-08-23) Columbus, Ohio, US; abstract no. 51068r, H.SAITO: "Porous inorganic building material" XP000183229 abstract & JP 51 036217 A (TEIJIN, LTD) 27 March 1976 (1976-03-27) --- -/--	1,8, 10-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *P* document published prior to the international filing date but later than the priority date claimed

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- *Z* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Int'l Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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Information on patent family members

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